SHORT COMMUNICATION

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Radiotracer study of the adsorption of sulfate ions at a Bi$_2$O$_3$ powder/electrolyte solution interface

Abstract The pH and concentration dependence of the adsorption of sulfate ions on powdered Bi$_2$O$_3$ was studied by a radiotracer technique in the presence of a large excess of perchlorate supporting electrolyte. It was found that, similar to other oxides such as Al$_2$O$_3$, Cr$_2$O$_3$ and Fe$_2$O$_3$, the extent of adsorption is determined by the protonation of the Bi$_2$O$_3$ surface. The redox transformations of Bi adatom layers are discussed in the light of the results obtained. It is established that for the interpretation of the redox processes occurring at the Bi/electrolyte interface the role of protonation of the oxide formed and the anion adsorption induced by the oxide layer should be taken into consideration.

Keywords Bismuth oxide · Radiotracer technique · Specific adsorption · Sulfate ions

Introduction

Bismuth oxide is a component of various mixed oxides or oxide layers of practical importance (superconductors, rechargeable battery materials, etc.). On electrode catalysts modified by Bi adatoms the Bi species are present mostly in oxidized form. Even the study of Bi adatom layers shows that the voltammetric behavior of these layers is determined by the reversible oxidation/reduction of Bi adatoms (see [1, 2, 3, 4, 5, 6, 7, 8] and literature cited therein).

Considering, for instance, the latter phenomena, clarification of the role of anion adsorption could be an important point for the elucidation of the mechanism of the redox transformations occurring at the Bi/electrolyte interface. Thus, investigation of the adsorption of anions on Bi$_2$O$_3$ could be considered as a contribution to the study of the Bi/Bi$_2$O$_3$ system in electrolyte solutions. In a recent communication [9], a cyclic voltammetric study of bismuth oxide powder by means of a cavity microelectrode coupled with Raman microspectrometry has been carried out. The species involved in the redox transformation were identified. On the basis of the results obtained it was concluded that bismuth oxy-hydroxides and not Bi$_2$O$_3$ should be considered as the electroactive species.

The radiotracer method used for the study of the sorption of anions on various powdered oxides (Al$_2$O$_3$, Fe$_2$O$_3$, ZnO, CuO and Cr$_2$O$_3$) [10, 11, 12, 13, 14, 15, 16, 17, 18, 19] can be applied without any problem to the case of Bi$_2$O$_3$ powder as well. The aim of the present work is to report the results of the study of the specific adsorption of radiolabeled sulfate ions at powdered Bi$_2$O$_3$. This work can be considered as a continuation of the radiotracer studies on the sorption behavior of Bi adatom layers on a platinized platinum electrode [20]. An attempt will be made to compare the results obtained for Bi$_2$O$_3$ with those available for Bi adatoms.

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Experimental

The experimental technique and set-up for the radiotracer study of the sorption processes have been described and presented in previous papers [10, 11, 12, 13, 14, 15, 16]. The main principle of the method [17] used in the present study consists of the measurement of the radiation intensity originating from solution species adsorbed on a powdered oxide layer sprinkled on a thin plastic foil. This foil serves, simultaneously, as the window for radiation measurement. The measurements were carried out at ambient temperature in an argon atmosphere. The argon purge of the solution was directed through the gap between the bottom of the measuring cell and the detector. ^{35}S-labeled H$_2$SO$_4$ (Amersham, specific activity 200 MBq mmol^{-1}) was used for study of the sulfate adsorption. Generally, the amount of Bi$_2$O$_3$ referred to the geometric surface area of the bottom of the cell was 20–30 mg cm^{-2}. This thickness of the Bi$_2$O$_3$ layer can be considered as infinite with respect to the depth of propagation of the soft β radiation of ^{35}S.

In most of the experiments, concentration of the labeled species was at least by one order of magnitude lower than that of the supporting electrolyte (NaClO$_4$ or/and HClO$_4$) in order to determine the specific adsorption of these compounds on the oxide surface. The pH of the solutions was adjusted by addition of HClO$_4$ or NaOH.

A commercial Bi$_2$O$_3$ powder (Reanal) was used. As the aim of the present study was only to clarify the main trends of behavior, and not to study the specific properties of a particular Bi$_2$O$_3$, no effort was undertaken to obtain more physical data characterizing the Bi$_2$O$_3$ powder.

The combined radiometric and voltammetric study of anion adsorption on Bi adatoms was carried out by the technique described previously [17, 20].

Results and discussion

pH and concentration dependence of the adsorption of sulfate ions

Similar to the earlier studies carried out with other oxides [11, 12, 13, 14, 15, 16], the first experiments of the present work were aimed at the determination of the pH dependence of the specific adsorption of sulfate ions in order to obtain information on the pH range in which measurable adsorption occurs. These studies were performed for the 0.5 mol dm^{-3} NaClO$_4$ supporting electrolyte at low sulfate concentrations ($c < 10^{-3}$ mol dm^{-3}), as required for the determination of specific adsorption without interference of electrostatic effects. The pH was adjusted by addition of HClO$_4$ or NaOH.

In a previous communication [10] it was shown that the possible slow dissolution rate of an oxide layer of 30 mg cm^{-2} does not distort the study of specific adsorption of sulfate ions, even in the presence of 1 mol dm^{-3} HClO$_4$ (pH$\approx$0).

Figure 1 shows the pH dependence of the count rate versus pH curve. The shape of this curve is close to those obtained for CuO [18], Cr$_2$O$_3$ [19], Fe$_2$O$_3$ [11] and Al$_2$O$_3$ [12]. This type of behavior was interpreted in terms of the protonation of the oxide surface, characterized by an equilibrium formulated by the equation:

$$X + H^+ \rightleftharpoons XH^+ \qquad (1)$$

where X is a surface site. The tendency to attain a limiting value of the surface protonation is also in accordance with observations made with other oxides.

In the case of equilibrium:

$$k_a c_{H^+}(1 - \theta_{H^+}) - k_d \theta_{H^+} = 0 \qquad (2)$$

where k_a and k_d are the rate constants of adsorption and desorption, respectively, and:

$$K c_{H^+} = \frac{\theta_{H^+}}{(1 - \theta_{H^+})} \qquad (3)$$

where:

$$K = \frac{k_a}{k_d} \qquad (4)$$

is the proton equilibrium constant and θ_{H^+} is the coverage with respect to the protonated surface sites. For:

$$\frac{\theta_{H^+}}{1 - \theta_{H^+}} = 1 \qquad (5)$$

$$\log K = pH \qquad (6)$$

Thus, one can estimate the value of the protonation equilibrium constant from the count rate versus pH curve (see [11, 12]). Taking into consideration the data presented in Fig. 1, one can estimate the log K value as being ca. 5.5.

The concentration dependence of the adsorption of sulfate ions (expressed as count rate) was determined at pH = 1.0 in the presence of the 0.5 mol dm^{-3} (NaClO$_4$ + HClO$_4$) supporting electrolyte. The results obtained are presented in Fig. 2. A similarity of the behavior of the system studied to those of other oxides is
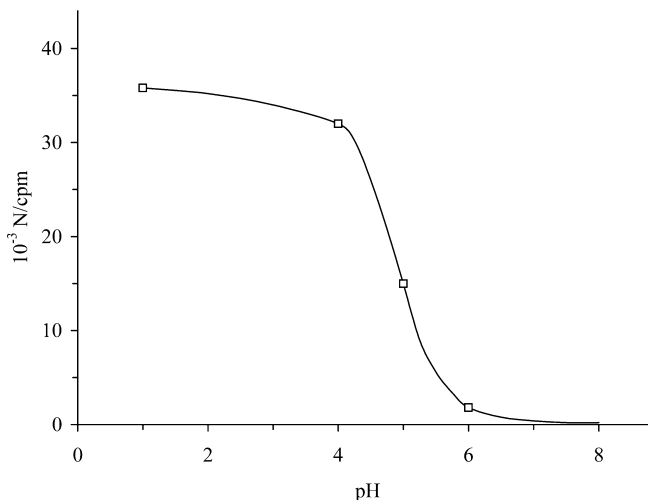

Fig. 1 pH dependence of the adsorption of labeled sulfate ions (expressed as count rate) on a Bi$_2$O$_3$ powder (30 mg cm^{-2}) in 2×10^{-4} mol dm^{-3} labeled H$_2$SO$_4$ with 0.5 mol dm^{-3} NaClO$_4$ supporting electrolyte. The pH was adjusted by addition of HClO$_4$ or NaOH
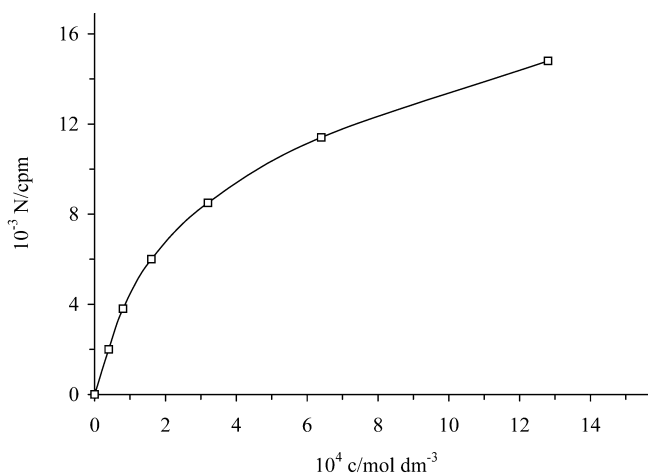

Fig. 2 Concentration dependence of the adsorption of labeled sulfate ions in 0.5 mol dm^{-3} (NaClO$_4$ + HClO$_4$) at pH 1.0

evident [11, 12] (Langmuir-like adsorption isotherm showing a limiting value at moderate concentrations). The $1/N$ versus $1/c$ plot gives a linear relationship, supporting the Langmuir-like behavior.

The interpretation of the behavior of oxides on the basis of Eq. 1 seems oversimplified considering, for instance, the MUltiSIte Complexation (MUSIC) model [21, 22, 23, 24] or the thermodynamic approach suggested by Petrii [25]. However, the latter refers to oxides with metallic conductivity (iridium dioxide, ruthenium dioxide), while in the case of the MUSIC model the role of double layer (electrostatic) effects are taken into consideration. As mentioned, in our work, owing to the great excess of supporting electrolyte, only the specific adsorption is measured without any contribution from electrostatic effects. Similar studies with various oxides [10, 11, 12, 13, 14, 15, 16, 17, 18, 19] show that the experimental results are in acceptable agreement with Eq. 1.

Study of the reversibility of the adsorption of sulfate ions

The "mobility" of the adsorbed ions is an important issue when describing the adsorption phenomena in terms of isotherms. In order to describe unambiguously the adsorption equilibrium or equilibrium states with respect to the adsorbed species, the investigation of their desorption rates is of primary importance.

The study of the exchange of labeled adsorbed sulfate ions with those non-labeled and added, in a large excess, to the solution phase, reveals that the adsorbed sulfate ions are loosely bound to the Bi_2O_3 surface. This effect is demonstrated in Fig. 3. In this figure it may be seen that the addition of non-labeled SO_4^{2-} results in a rapid decrease in the count rate.
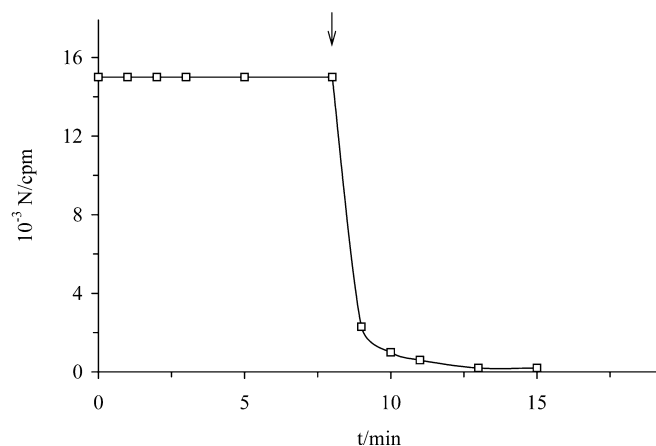
Conclusions and comparison with data obtained for an electrodeposited Bi layer and Bi adatoms on a platinized platinum electrode

The experimental results presented above clearly demonstrate that significant anion-specific adsorption can be observed on a protonated Bi_2O_3 surface. This fact should be taken into consideration for the evaluation of adsorption data obtained with metallic Bi (electrodeposited layer) and Bi adatoms formed, for instance, on platinum or platinized platinum electrodes.

From the coupled radiotracer adsorption and voltammetric study of Bi adlayers on platinized platinum electrodes, it was concluded that the formation of surface oxides plays a predominant role in the specific adsorption of anions on the Bi adlayer. The voltammetric behavior of the adlayer is presented in Fig. 4, while in Fig. 5 the potential dependence of the specific adsorption of sulfate species is shown (the principle of the determination of the adsorption is the same as for oxides; however, in the former case the bottom of the cell is a gold plated and platinized plastic foil [20]).

The voltammetric curve shows the well-known redox behavior explained by the formation and reduction of the bismuth oxide layer. Anion-specific adsorption can be observed only in this potential range, although in the absence of Bi^{3+} ions a significant adsorption of anions occurs on the support at potentials preceding the potential values corresponding to this redox process [20]. This means that, on the metallic adatom layer, no specific adsorption of the anions occurs. It has been stated [20] that the increase in anion adsorption takes place only at potentials where the oxidation of the adatom layer becomes more and more pronounced. Thus the potential dependence of the adsorption of anions on the Bi adlayer reflects the potential dependence of the coverage with respect to the protonated bismuth oxide active in the anion adsorption.

It is evident that these facts cannot be omitted from considerations of the interpretation of voltammetric and electrochemical quartz crystal microbalance data
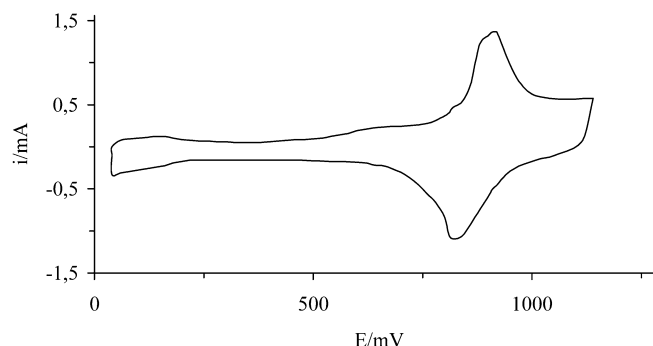

Fig. 3 Exchange of labeled adsorbed sulfate ions with non-labeled ions added to the solution in a large excess (in the form of H_2SO_4) at an instant indicated by the *arrow*; initial and final SO_4^{2-} concentrations were 2×10^{-4} and 4×10^{-2} mol dm^{-3}, respectively. Supporting electrolyte was 0.5 mol dm^{-3} (NaClO$_4$ + HClO$_4$), pH 1

Fig. 4 Voltammetric curve of a platinized electrode obtained in the presence of 5×10^{-5} mol dm^{-3} Bi^{3+} in 1 mol dm^{-3} H_2SO_4 supporting electrolyte in the potential range from 40 to 1050 mV; sweep rate 1 mV s^{-1}; RHE scale
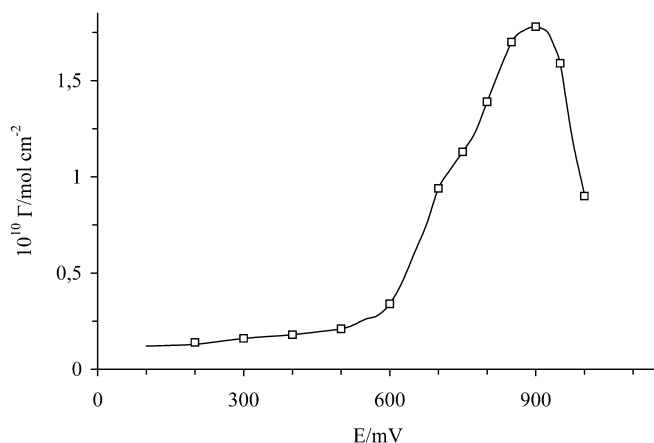
Fig. 5 Equilibrium potential dependence (RHE scale) of the adsorption of HSO_4^- (SO_4^{2-}) ions on a platinized electrode in the presence of Bi^{3+} ions (5×10^{-5} mol dm^{-3}) in 1 mol dm^{-3} $HClO_4$; $c_{H_2SO_4} = 5 \times 10^{-5}$ mol dm^{-3}

obtained with Bi adlayers. Fortunately, the charge balance of the surface oxidation/reduction presumably is not influenced significantly by the anion adsorption, as this latter process takes place following the protonation of the surface.

The positive charge of the H^+ ions involved in the protonated oxide layer will be partly or wholly compensated by the negative charge of specifically adsorbed anions. Thus the overall process can be considered as the specific adsorption of an electrically neutral species.

The problem of mass balance is more complicated. The adsorption of anions should be an important factor in determining the total mass change during the formation and reduction of the oxide layer. As the degree of protonation of the surface, and consequently the extent of anion adsorption, depends on the pH, so the mass change characteristic for the formation of the oxide layer should also depend on the pH of the solution phase. It is hoped that the observations and conclusions presented here may contribute to a better understanding of the systems considered.

Finally, in connection with the comparison of the behavior of Bi_2O_3 and Bi adatoms, it should be noted that from a thermodynamic point of view the comparison is not completely justified as Bi adatoms do not form any phase, while the Bi_2O_3 powder layer can be considered as an independent phase. In addition, in contrast to Bi adatoms, in the case of Bi_2O_3 the adsorption measurements were done in the absence of potential control (however, this problem follows from the very low conductivity of Bi_2O_3).

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